and condenser was added a cold solution of 10 g. of ethyl-2-C^{14} chloride (0.825 μc./mmole) in 27 g. of benzene. The mixture was heated at reflux for 1.25 hours and hydrolyzed with water. The washed and dried benzene layer was distilled through a 100-cm. Vigreux column. The collected ethylbenzene fraction, boiling at 133–135°, weighed 4.1 g. or 25% of theoretical. Degradation of the ethylbenzene by the procedure described above gave non-radioactive benzoic acid.

Isomerization of Ethyl-2-C^{14} Chloride.—A 20-g. portion of ethyl-2-C^{14} chloride (0.825 μc./mmole) was transferred in a vacuum line onto 2 g. of solid aluminum chloride. The mixture was quickly brought to room temperature and atmospheric pressure and allowed to stand at room temperature for one hour. At the end of this time the product was distilled *in vacuo* through a trap containing potassium hydroxide pellets to remove hydrogen chloride. The product was distilled several times at atmospheric pressure and collected in a trap maintained at −80°. Uncondensed gases such as ethylene were removed. Finally the gas was passed through bromine water, a "Drierite" trap, and condensed. Distilled at atmospheric pressure, the product weighed 9.3 g., b.p. 12° (743 mm.).

The isomerized ethyl chloride was condensed with benzene in the presence of aluminum chloride as described above. The resultant ethylbenzene was degraded to benzoic acid which was assayed for radioactivity. Samples weighing 19.51 and 17.70 mg. had radioactivities of 0.0551 and 0.0503 μc., respectively. Since the millimolar activity was thus 0.345 microcurie, the percentage isomerization was 83.6%.

A previous experiment which was not quite so carefully carried out and which involved the isomerization of 12 g. of ethyl-2-C^{14} chloride over 7.5 g. of aluminum chloride revealed 92% isomerization of the ethyl chloride.

Radioactivity Measurements.—Determinations of radioactivity were made on 5- to 20-mg. samples of purified organic compounds by wet combustion of the sample and ion chamber–vibrating reed electrometer measurement of the resulting carbon dioxide. The method which is previously described[23] is subject to an error of less than ±1%.

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[23] O. K. Neville, This Journal, **70**, 3501 (1948).

Oak Ridge, Tennessee

[Contribution from the Department of Chemistry, University of Florida]

The Course of the Reaction of 1,4- and 1,5-Dihalo- and Di-(arylsulfonoxy)-alkanes with Diallylamine

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In attempting to prepare 1,4-bis-(diallylamino)-butane and 1,5-bis-(diallylamino)-pentane by reaction of the 1,4- and 1,5-dihalo- and di-(arylsulfonoxy)-alkanes with diallylamine, neither of the desired products was obtained. In the presence of an excess of diallylamine, the products of the reaction were allylpyrrolidine and triallylamine from the 1,4-derivatives, and allylpiperidine and triallylamine from the 1,5-derivatives. The products of the reaction can be explained on the basis of an intramolecular cyclization to the five- or six-membered cyclic quaternary ammonium salt, followed by allylation of the excess diallylamine by the quaternary ammonium salt to produce triallylamine and the appropriate allyl-substituted heterocyclic amine. In order to check this proposed mechanism, diallylpyrrolidinium bromide was prepared and heated with diallylamine, resulting in the formation of allylpyrrolidine and triallylamine. The reaction products were identified by both chemical means and by infrared spectral analysis. The desired compounds were obtained by reduction of the corresponding amides with lithium aluminum hydride.

In preparing a series of unsaturated quaternary ammonium salts of the structure

$$Br^-R_3{}^+N(CH_2)_nN^+R_3Br^-$$

in which $n = 2$–10, it became necessary to prepare the corresponding bis-(diallylamino)-alkanes as intermediates. For those compounds in which n = 2, 3 or 6–10, acceptable yields were obtained by one of the following methods: (1) reaction of the 1,X-dihaloalkane with diallylamine in presence of sodium carbonate or (2) the method of Laakso and Reynolds[2] which employs the reaction of the di-(arylsulfonates) of the corresponding glycols with diallylamine. Although these authors reported acceptable yields of 1,4- and 1,5-bis-(dialkylamino)-alkanes by this procedure, use of this method, as well as method 1, in attempts to prepare 1,4-bis-(diallylamino)-butane and 1,5-bis-(diallylamino)-pentane did not prove satisfactory.

This paper deals with the isolation and identification of the products of the above reactions when applied to the 1,4- and 1,5-derivatives. On the basis of previously reported data[3] and on data obtained in this study, an explanation is given for the course of the reaction.

Experimental

Reaction of 1,4-Dibromobutane with Diallylamine.—(1) A mixture of 44.5 g. (0.206 mole) of 1,4-dibromobutane, 60 g. (0.618 mole) of diallylamine, 34.6 g. of sodium bicarbonate and 20 ml. of water was refluxed for seven hours. After filtration and addition of sodium hydroxide to the filtrate, the organic layer was distilled; however, no material was obtained boiling in the expected range for 1,4-bis-(diallylamino)-butane.

(2) To 4 ml. of 1,4-dibromobutane was added 12 ml. of diallylamine at a temperature of 35°. While the liquid was being stirred, the temperature rose to 100°. After standing overnight, the crystalline product was collected and washed with acetone; m.p., decomposition at 205°, liquid at 315–322°.

Anal. Calcd. for $[(CH_2{=}CHCH_2)_2N^+H(CH_2)_4N^+H(CH_2CH{=}CH_2)_2]2Br^-$: Br, 38.98. Calcd. for diallylpyrrolidinium bromide: Br, 34.49. Found: Br, 34.77.

Since diallylpyrrolidinium bromide has not been reported previously in the literature, it was prepared as follows:

To a cold mixture of 21.0 g. (0.19 mole) of N-allylpyrrolidine (b.p. 129–130°, n^{25}_D 1.4486) and 75 ml. of acetone was added carefully 25.0 g. (0.207 mole) of allyl bromide with cooling. The hygroscopic compound which precipitated was washed with acetone; yield 39.0 g., 90.5%; m.p., decomposition at 202°, melted at 315–320°; mixed m.p. with above compound, decomposition at 198°, melted at 314–322°.

Since adequate physical constants could not be found in the literature on allylpyrrolidine, it was prepared by treating pyrrolidine with allyl bromide in the presence of sodium carbonate; b.p. 129–130°, n^{25}_D 1.4486.

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[1] Abstracted from a dissertation to be presented by Rudolph J. Angelo to the Graduate School of the University of Florida in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] T. M. Laakso and D. D. Reynolds, This Journal, **73**, 3518 (1951).

[3] E. L. Eliel and P. E. Peckham, *ibid.*, **72**, 1209 (1950).

Anal. Found C, 75.3; H, 11.87; N, 12.41. Calcd. for $C_7H_{13}N$: C, 75.6; H, 11.71; N, 12.61.

Reaction of 1,5-Dibromopentane with Diallylamine.—A mixture of 4 ml. of 1,5-dibromopentane and 12 ml. of diallylamine was allowed to stand overnight. The hygroscopic crystals were collected and washed with acetone; m.p. 194–196° dec. Diallylpiperidinium bromide has flash m.p. of 190°.[4]

Anal. Calcd. for $[(CH_2{=}CHCH_2)_2N(CH_2)_5N(CH_2CH{=}CH_2)_2]\cdot 2HBr$: Br, 37.75; Calcd. for diallylpiperidinium bromide, $C_{11}H_{20}NBr$: Br, 32.4. Found: Br, 32.84.

Reaction of 1,4-Di-(*p*-toluenesulfonoxy)-butane with Diallylamine.—After a number of unsuccessful attempts to obtain 1,4-bis-(diallylamino)-butane by the method of Laakso and Reynolds,[2] the following modification was adopted: 1,4-Di-(*p*-toluenesulfonoxy)-butane 228 g. (0.577 mole), and 632 g. (6.5 moles) of diallylamine were refluxed for 72 hours. The mixture was allowed to cool and the layers separated. The lower layer was treated with an excess of 40% sodium hydroxide solution, allowed to stand overnight and filtered. From the filtrate, 3 g. of a yellow liquid, b.p. 100–110° (0.5–0.3 mm.), n^{24}D 1.4721, was obtained. Diallylamine, 180 g., was recovered, and the remaining liquid was distilled at reduced pressure. A light yellow liquid, 11.5 g., b.p. 100–110° (0.3–0.5 mm.), n^{24}D 1.4720, was obtained. *Anal.* Found: N, 9.38. Calcd. for $C_{16}H_{28}N_2$: N, 11.27. These fractions appear to be impure 1,4-bis-(diallylamino)-butane, as this compound was prepared by another method and found to have b.p. 96–98° (0.1 mm.), and n^{23}D 1.4716. A large amount of material which collected in the cold trap was fractionated. A small amount of diallylamine was recovered, followed by 20 g., boiling range 111–147°, and 21 g. having b.p. 147–149°, n^{25}D 1.4489. With allyl bromide, it gave tetraallylammonium bromide, m.p. 183–184°; mixed m.p. with an authentic sample, 182–183°; reported b.p. of triallylamine, 148–149°, n^{25}D 1.4502. The intermediate fraction should contain allylpyrrolidine if the above proposed mechanism is correct.

Reaction of Diallylpyrrolidinium Bromide with Diallylamine.—In order to support the above proposed course for the reaction, 36.0 g. (0.155 mole) of diallylpyrrolidinium bromide and 120.0 g. (1.24 moles) of diallylamine were refluxed for 36 hours. During this time, the liquid temperature remained at 109°, the b.p. of diallylamine. After this time, the salt became viscous and the color changed to light red. The temperature rose to 120°. Refluxing was continued for 12 hours. The mixture was cooled, filtered and the dark red solution fractionated to yield diallylamine, 68 g., b.p. 110–113°, u^{25}D 1.4397; allylpyrrolidine, 7 g., b.p. 130–140°, n^{25}D 1.4471; and triallylamine, 4.5 g., b.p. 146–149°, n^{25}D 1.4499.

Treatment of the allylpyrrolidine with allyl bromide gave the quaternary ammonium salt, m.p. 313–320° dec.; mixed m.p. with an authentic sample, 314–321° dec. The triallylamine was treated with allyl bromide to give the quaternary ammonium salt, m.p. 184–185°; mixed m.p. with an authentic sample. 184–185°.

Reaction of 1,5-Di-(benzenesulfonoxy)-pentane with Diallylamine.—1,5-Di-(benzenesulfonoxy)-pentane, 279 g., and 776 g. of diallylamine were refluxed with stirring for 48 hours. The product was separated as described above, and the excess diallylamine removed by distillation. Following the diallylamine, 45 g. of a colorless liquid boiling at 147–149° was obtained; no higher boiling material was obtained. After refractionation, a product, b.p. 148–150°, n^{25}D 1.4539, was obtained. On the basis of the above proposed mechanism for the reaction, this product should be a mixture of triallylamine, b.p. 148–149°, n^{25}D 1.4502, and allylpiperidine, b.p. 148–150°, n^{25}D 1.4577. Since it was impossible to separate these compounds by distillation, an infrared analysis was made using a Perkin–Elmer double beam infrared spectrophotometer, and cell thickness of 0.025 mm. A mixture of pure samples of triallylamine and allylpiperidine containing 51% by weight of triallylamine was prepared; this mixture had n^{25}D 1.4533.

INFRARED SPECTRAL ANALYSIS

Sample	n^{25}D	Absorption bands, μ				
Triallylamine	1.4502	3.38	9.32	..	..	..
Allylpiperidine	1.4577	..	..	7.23	7.70	8.33
Above mixture	1.4533	3.38sh	9.35	7.22	7.70	8.33
Reacn. product	1.4539	3.38sh	9.35	7.22	7.70	8.33

These results show conclusively the presence of both triallylamine and allylpiperidine, and the refractive index indicates approximately equal molar quantities of the two compounds.

Preparation of 1,4-Bis-(diallylamino)-butane.—After unsuccessful attempts to obtain this compound by the above procedures, the following method was adapted:

(1) **Preparation of N,N,N′,N′-Tetraallylsuccinamide.**—To a well-stirred mixture of 211 g. (2.168 moles) of diallylamine and 200 ml. of benzene was added a solution of 84 g. (0.542 mole) of succinyl chloride in 100 ml. of benzene, the temperature being maintained at 10–20°. Stirring was continued at this temperature for one hour. The solution was filtered and the diallylamine hydrochloride washed with dry benzene. After removal of the benzene, the residue was distilled under reduced pressure to obtain 100 g. of liquid, b.p. 157–165° (0.08–0.1 mm.), n^{24}D 1.5025, d^{25}_4 1.0060. The infrared spectrum showed absorption bands for amide, carbonyl and carbon–carbon double bond; yield 80.6%.

Anal. Found: C, 69.0; H, 9.14; N, 9.7; *MR*D, 81.86. Calcd. for $C_{16}H_{24}O_2N_2$: C, 69.5; H, 8.8; N, 10.1; *MR*D, 81.15.

(2) **Reduction of N,N,N′,N′-Tetraallylsuccinamide.**—To 16 g. of lithium aluminum hydride and 300 ml. of dry ether in a 3-l. 3-neck flask equipped with ice-water condenser, thermometer, dropping funnel and sealed stirrer, and cooled in an ice-bath, was added during 1.75 hours, 62 g. (0.225 mole) of tetraallylsuccinamide dissolved in 200 ml. of dry ether. The temperature was maintained below 15° during the addition. After refluxing 50 hours, a mixture of ethanol and water was added to destroy the excess lithium aluminum hydride. The mixture was then treated with 800 ml. of 10% sodium hydroxide solution, and solid sodium hydroxide added until the liquid separated into two layers. The ether layer was separated and the water layer extracted twice with 200-ml. portions of ether. The ether layers were dried over solid sodium hydroxide, and the ether removed. The residue was distilled under reduced pressure to yield 27.5 g. (49.3%), b.p. 96–98° (0.1 mm.), n^{23}D 1.4716. The infrared spectrum of the compound showed the absence of the carbonyl band and presence of carbon–carbon double bond band.

Anal. Found: C, 77.5; H, 11.3; N, 10.7. Calcd. for $C_{16}H_{28}N_2$: C, 77.4; H, 11.3; N, 11.2.

This compound was converted to 1,4-bis-(methyldiallylammonium)-butane dibromide, m.p. 163–165°, by treating with methyl bromide.

Anal. Found: Br, 36.41. Calcd. for $C_{18}H_{34}N_2Br_2$: Br, 36.47.

Preparation of 1,5-Bis-(diallylamino)-pentane. (1) **Preparation of N,N,N′,N′-Tetraallylglutaramide.**—Using 64 g. (1.64 moles) of diallylamine and 72 g. (0.425 mole) of glutaryl chloride, and following the procedure described above for tetraallylsuccinamide, 113 g. (91.7%) of tetraallylglutaramide was obtained; b.p. 165–167° (0.02 mm.), n^{25}D 1.5020.

Anal. Found: C, 69.9; H, 8.86; N, 9.26. Calcd. for $C_{17}H_{26}O_2N_2$: C, 70.3; H, 8.86; N, 9.65.

The infrared spectrum showed absorption bands for amide, carbonyl and carbon–carbon double bond.

(2) **Reduction of N,N,N′,N′-Tetraallylglutaramide.**—Using 21 g. (0.553 mole) of lithium aluminum hydride and 87 g. (0.30 mole) of tetraallylglutaramide, and following the procedure described above for the reduction of tetraallylsuccinamide, with the exception that this solution was allowed to stir four hours instead of reflux 50 hours, 53 g. (67.4%), b.p. 96–97° (0.02 mm.), n^{22}D 1.4743, was obtained. The infrared spectrum showed the absence of the carbonyl band and the presence of a strong terminal carbon–carbon double bond band. Several derivatives are recorded in Table I.

Anal. Found: C, 77.3; H, 11.24; N, 10.33. Calcd. for $C_{17}H_{30}N_2$: C, 77.8; H, 11.46; N, 10.68.

TABLE I

DERIVATIVES OF 1,5-BIS-(DIALLYLAMINO)-PENTANE

Reactant	M.p., °C.	Bromine, % Calcd.	Bromine, % Found
Methyl bromide	193–194 d.	35.34	35.36
Allyl bromide	154–155	31.69	31.72
Hydrogen bromide	115–117	37.66	37.58

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(4) G. B. Butler and R. L. Bunch, THIS JOURNAL, **71**, 3120 (1949).

Discussion of Results

In the reaction of 1,4- or 1,5-dihaloalkanes with diallylamine, it appears likely that the first attack would result in formation of the 4- or 5-bromoalkyl diallylamine hydrobromide. In the presence of an excess of diallylamine, the free bromoalkyl diallylamine should be liberated. The second step probably involves cyclic quaternary ammonium salt formation. It has been pointed out[5] that aliphatic bases containing amine and halogen in the 1,4-positions exist only as a salt and on liberation of the base condense to pyrrole derivatives. It has also been shown[6] that amines of the type $X(CH_2)_nNR_2$ yield $(CH_2)_n\overset{+}{N}R_2X^-$ when n has a value of 4, 5 or 6. Although disproportionation was not observed in the reaction of diallylamine with either 1,4-dibromobutane or 1.5-dibromopentane, probably because a large excess of diallylamine was not used, when diallylpyrrolidinium bromide was heated with a large excess of diallylamine, both allylpyrrolidine and triallylamine were isolated and identified. This disproportionation also occurred in attempting to use the method of preparation which involved use of the di-(arylsulfonoxy)-alkanes with a large excess of diallylamine. Although Laakso and Reynolds[2] reported a yield of 77.5% in the preparation of 1,4-bis-(dibutylamino)-butane, and 66.5% in the preparation of 2,5-bis-(dimorpholino)-hexane, the yield was only 10% in the preparation of 1,5-bis-(dibenzylamino)-pentane. It has been shown by von Braun, Kuhn and Goll[7] that the relative firmness of attachment of hydrocarbon residues to heterocyclic nitrogen in quaternary ammonium salts increases in the following order: allyl, benzyl, methyl, ethyl, propyl, etc. These authors also pointed out that methyl groups were lost in presence of primary or secondary amines from quaternary ammonium salts of heterocyclic nitrogen compounds, even piperazine, the least stable heterocyclic nitrogen compound studied, without rupture of the ring. The fact that the partial ionic character of carbon bond attachments in allyl and benzyl compounds is greater than in alkyl compounds due to resonance resulting in increased stability of the resulting ions, probably accounts for the poor yield of 1,5-bis-(dibenzylamino)-pentane and tends to support the carbonium ion[3] as an intermediate in the disproportionation reaction. The fact that furfuryltrimethylammonium iodide reacts with piperidine[3] to give a 48% yield of N-furfurylpiperidine is evidence that relative firmness of attachment, as discussed by von Braun, Kuhn and Goll,[7] of furfuryl is less than that of methyl. The fact that this reaction proceeds to 48% completion in three hours at reflux (approximately 100°) while after 36 hours at 109°, diallylpyrrolidinium bromide had shown no signs of reaction, would indicate that the C–N bond in furfuryltrimethylammonium iodide has a greater degree of ionic character than the allyl-N bond in diallylpyrrolidinium bromide. This is also supported by the fact that the number of resonance forms of the furfurylcarbonium ion is greater than that of the allylcarbonium ion.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN]

Arylation of Unsaturated Systems by Free Radicals. I. Arylation of Alkylbenzenes

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When toluene, cumene and *t*-butylbenzene are attacked by phenyl radicals, mixtures of alkylbiphenyls are produced. For each hydrocarbon, the ratios of *ortho*, *meta* and *para* substitution are the same, regardless of whether the radical was generated from benzoyl peroxide, N-nitrosoacetanilide or 1-phenyl-3,3-dimethyltriazene. The percentage *para* substitution is roughly constant (20); the percentage *ortho* substitution decreases from toluene (60) to cumene (27) to *t*-butylbenzene (15). A substantial amount of bibenzyl is formed from toluene, together with a minor impurity which may be biphenyl (or diphenylmethane); cumene gives a much larger quantity of 2,3-dimethyl-2,3-diphenylbutane. Syntheses of the pure alkylbiphenyls are reported, together with improved methods for 3-bromobiphenyl and indazole.

At the inception of this work, the orienting influence of a substituent on an aromatic ring toward an incoming aryl "free radical" was incompletely understood. As a result of the early work summarized by Bachmann and Hoffman,[3] it appeared that almost any substituent was a *para* director. However, this conclusion was based upon isolation of the *p*-substituted biphenyl and the inability of the earlier workers to isolate the pure *o*- and *m*-isomers in most cases. Since 1950, several workers[4-8] have been active in showing that each of the three isomers is formed. In fact, their results indicate that usually *ortho* substitution is predominant (50–60%) and that the *meta* and *para* isomers are formed in

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[1] Abstracted from a portion of the Ph.D. Dissertation of Harry S. Blanchard, University of Michigan, 1954.

[2] Allied Chemical and Dye Corporation Fellow, 1953–1954.

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